Geometrical and Orientational Isomers of $[Fe_3(CO)_{12-n}L_n]$ (n = 1–3)

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A detailed analysis of the structures of the potential isomeric forms of $[Fe_3(CO)_{12-n}L_n]$ (n = 1–3) has been performed. According to the ligand polyhedral model these structures are best visualised on the basis of mono-, bis- and tris-substituted icosahedral ligand shells. Both the bis- and the tris-substituted icosahedra exist in several forms. For bis substitution there are three forms, *viz.* the 1,2, the 1,7 and the 1,12 and for tris substitution there are the forms 1,2,3, 1,2,4, 1,x,12, 1,7,8 and 1,7,9 (x = 2–11). The mechanisms by which both fluxionality and isomerisation may occur in these systems is described.

The determination of the structure of $[Fe_3(CO)_{12}]$, both in the solid and in solution, and the understanding of the factors which govern it has proven to be a classic study which has been recounted on many previous occasions (see *e.g.* ref. 1). Nevertheless, it continues to provide some considerable interest and the nature of $[Fe_3(CO)_{12}]$ and its various substituted derivatives in solution remains elusive. Recently, on the basis of some elegant ^1H and ^{31}P NMR spectroscopic studies, Mann and his co-workers[1] were able to shed considerable light on this longstanding problem. Nevertheless, despite these studies we believe that a clear and full understanding of the complexities of the structures of these molecules is lacking. In this paper we present ideas based on the ligand polyhedral model (LPM) which we believe go a long way towards simplifying this complex problem and, although in this case are applied specifically to $[Fe_3(CO)_{12-n}L_n]$ (n = 1–3), the principles are general to all cluster carbonyls and their derivatives.

Surprisingly little attention has been paid in the past to the isomerism which may be exhibited by cluster species of the type M_mL_n. This may be because of the frequently complicated relationship that exists between the central metal cluster unit M_m and the peripheral ligand shell L_n.[2–4] Whereas for small n at least isomerism in monomeric complexes ML_n is generally relatively easily understood and described, the higher values of n, frequently $\geqslant 12$, and the lower *overall* symmetries observed in cluster compounds make for difficulties in any comprehensive and simple appreciation of the relationship between cluster isomers and any fluxional motions they may undergo. In particular, we believe that problems have arisen because of the failure to observe, identify and, most importantly, recognise the large numbers of isomers that may exist for a given system and hence to appreciate the criteria under which the mechanisms of interconversion operate. For example, the comparatively simple monosubstituted derivative $[Fe_3(CO)_{11}(PPh_3)]$ can theoretically exist in (at least) twelve perfectly reasonable isomeric forms. Failure to observe a given isomer experimentally in this and other cases is not unexpected and may, for example, be due either to differences in the method employed in their preparation and/or their ability to undergo rapid interconversion. Nevertheless, each isomer may be of relevance to the chemistry of the molecule and should not be ignored without justification.

According to the LPM,[5] it is convenient to regard cluster structures as composed of two interdependent parts:[2–4,6–8] the central metal core of a defined geometry and the surrounding ligand polyhedron. The two parts of the molecule are bonded by essentially non-directional bonds and hence the barrier to rotation, one polygon or polyhedron (M_m) about the other (L_n), is, in general, small. Thus, the iron triangle within the $(CO)_{12}$ icosahedron of $[Fe_3(CO)_{12}]$ may occupy at least eighty reasonable orientations (see below). Of these, three structural types emerge as being independent and distinguishable, *viz.* the forms with C_{2v} [Fig. 1(*a*)], C_2 [Fig. 1(*b*)] and D_3 symmetry [Fig. 1(*c*)].

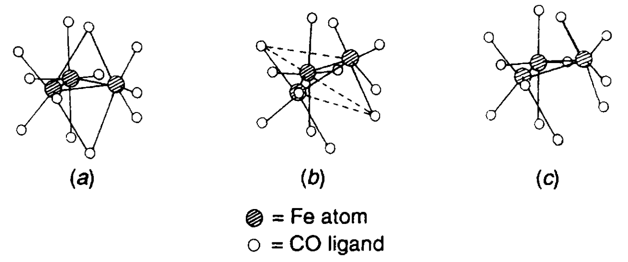
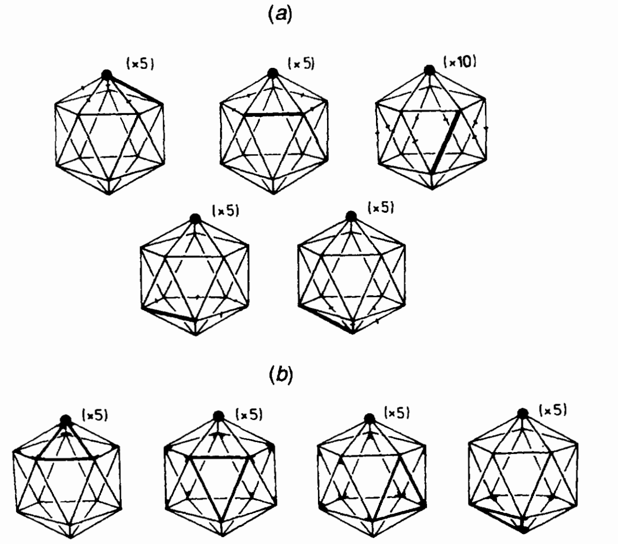


Fig. 1 Structures of $[Fe_3(CO)_{12}]$: (*a*) observed C_{2v} with two μ-CO bridges; (*b*) suggested C_2 with two μ_3-CO bridges; (*c*) D_3 with no CO bridges

In this paper we shall describe the various isomeric forms available to the mono-, bis- and tris-substituted derivatives of $[Fe_3(CO)_{12}]$ according to the ligand polyhedral model. We shall then explain how isomerisation can occur either by libration of the Fe_3 triangle within the quasi-icosahedral ligand envelope (or the converse) or by polyhedral interconversion through an anticubeoctahedral intermediate geometry. Brief details of some aspects of this work have been communicated previously.[2,6]

Isomers and Isomerisation

In Scheme 1 we list the orientational isomers available to $[Fe_3(CO)_{11}L]$. A key to the numbering and symmetry is shown in Fig. 2. All are based on a quasi-icosahedral arrangement of the twelve ligands and differ only in the arrangement of the Fe_3 triangle within the ligand shell. In Scheme 1(*a*) are given those structures which contain two μ-CO bridges and which are clearly derived from the idealised C_{2v} form of the $[Fe_3(CO)_{12}]$ established in the solid. Their valence-bond counterparts are also illustrated in Fig. 3 so that the structural relationships one to another are clearly seen. In Scheme 1(*b*) are listed those structures which, although still based on the quasi-icosahedral arrangement of ligands, contain only terminally bonded CO ligands and are derived from the alternative D_3 form of $[Fe_3(CO)_{12}]$ thought to exist in solution.[3] Again the valence-bond counterparts are included for comparison in Fig. 3. We shall not consider isomers based on the structure of



Scheme 1 Relationship between the orientational isomers of $[Fe_3(CO)_{11}L]$ based on a ligand polyhedron: (*a*) forms containing two bridges and based on the structures of $[Fe_3(CO)_{12}]$ in the solid (symmetry C_2 or C_{2v}); (*b*) forms based on the alternative D_3 form postulated for $[Fe_3(CO)_{12}]$ in solution

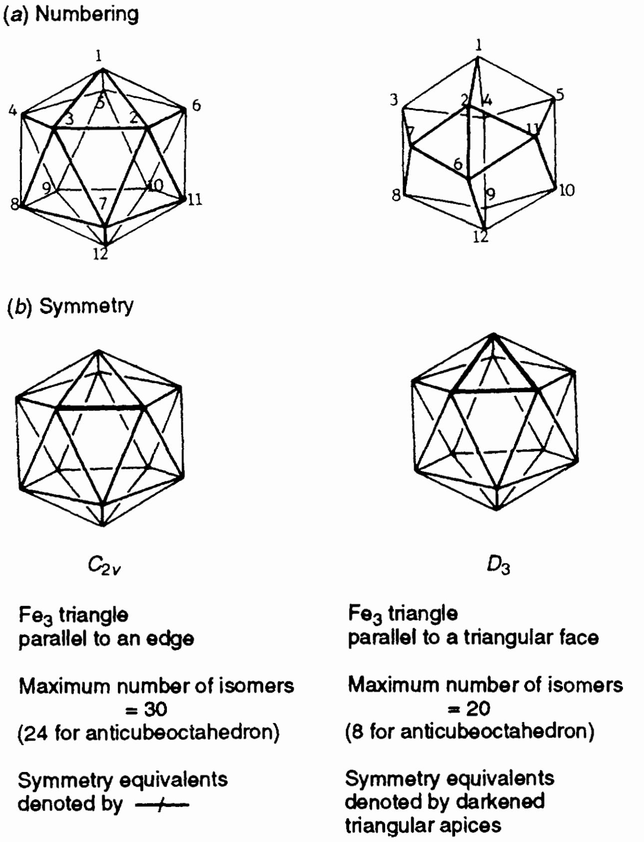


Fig. 2 Key to numbering scheme and symmetry in Schemes 1–5

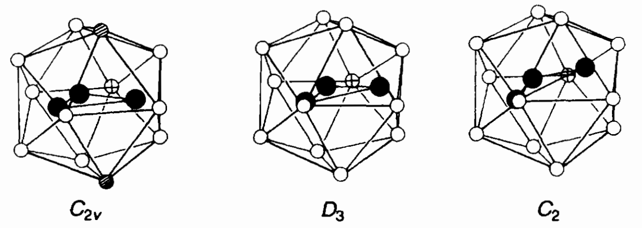


Fig. 3 Interconversion of three isomeric forms of $[Fe_3(CO)_{11}L]$ by libration. This low-energy process is the same in both solid and solution

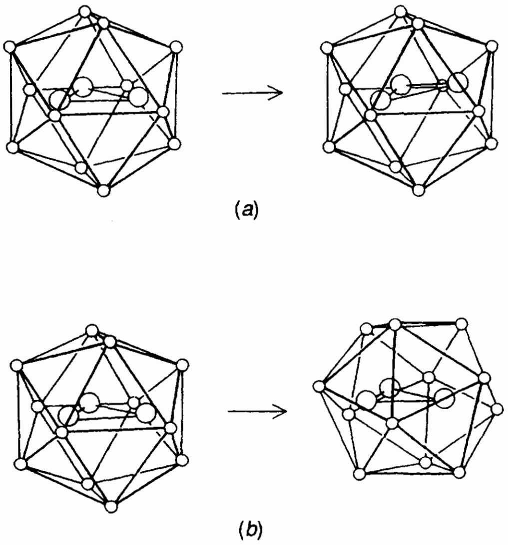


Fig. 4 (*a*) The libration of the Fe_3 triangle within the ligand polyhedron and (*b*) the rotation (or libration) of the icosahedron about a rigid Fe_3 triangle

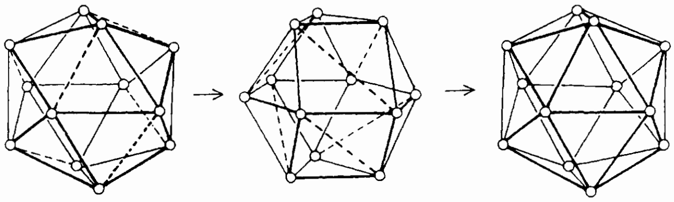


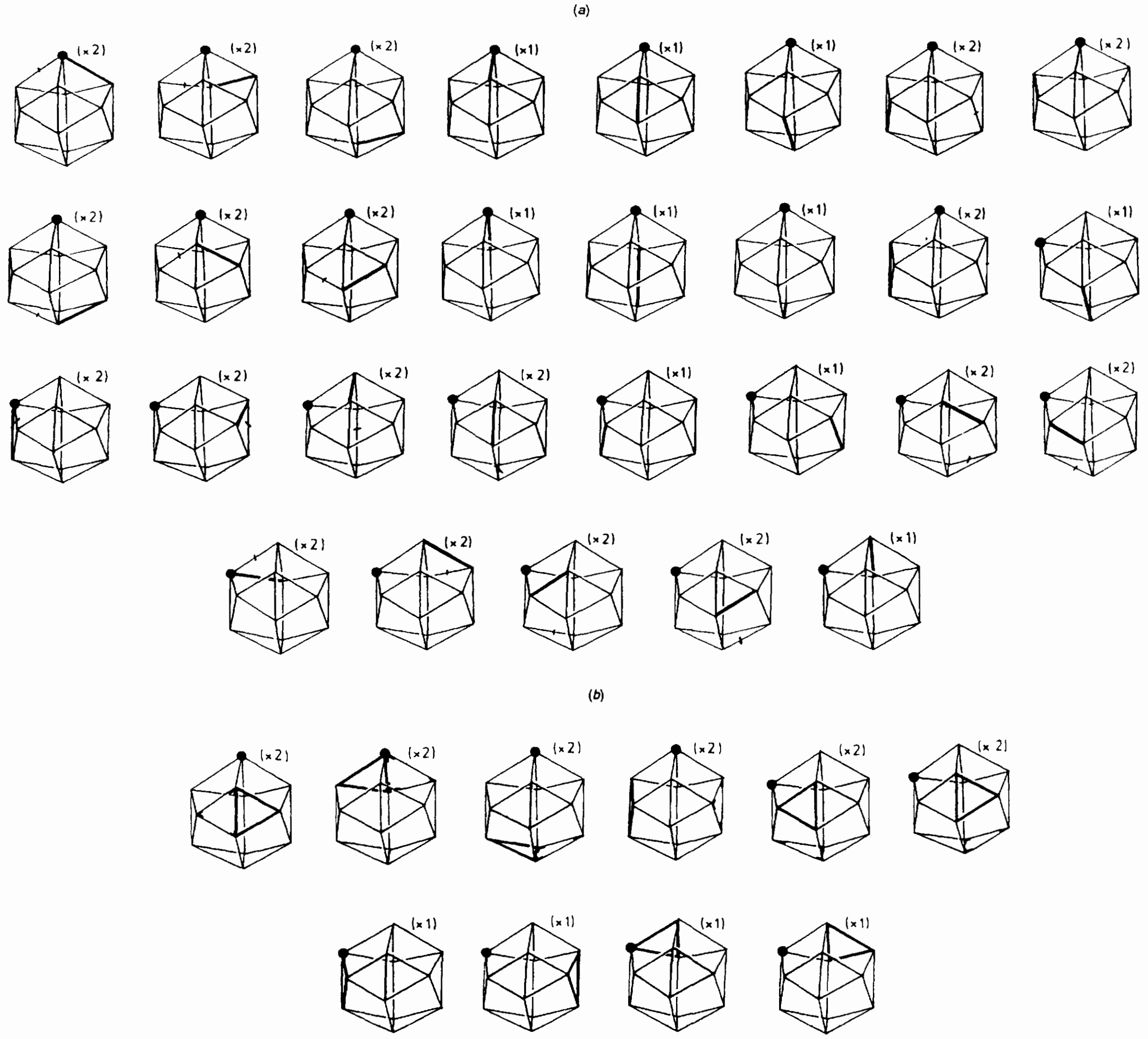
Fig. 5 Interconversion of the icosahedron into a 'new' icosahedron *via* the anticubeoctahedral complementary geometry; – – – – = edges broken or formed

$[Fe_3(CO)_{12}]$ with C_2 symmetry. They are expected to be similar to those of quasi-C_{2v} symmetry, but there is no direct evidence that they exist.

All those structures included in Scheme 1(*a*) and 1(*b*) are derived by the insertion of the Fe_3 triangle within the same quasi-icosahedral ligand envelope and differ only in the orientation of the Fe_3 triangle relative to that of the surrounding icosahedron. It follows that all may be interconverted from one to another simply by rotation (or libration) of the iron triangle within the icosahedron [see Fig. 4(*a*)] or, conversely, the movement of the icosahedron about a fixed Fe_3 triangle [see Fig. 4(*b*)]. Hence, we deem them to be orientational isomers. It is important to recognise that the act of libration does not necessitate the migration of L from one metal atom to another. The librational motion may retain the interaction of L with the same metal atom; it is the nature of L which varies.

In Scheme 2 we show an alternative set of structures based on the quasi-anticubeoctahedral arrangement of ligands. As we have stressed previously,[4,6] the anticubeoctahedron, or indeed its close relative the cubeoctahedron, is a less favourable ligand arrangement. Insertion of the Fe_3 unit into this polyhedron leads to a structure based on that observed[9] for $[Os_3(CO)_{12}]$ (with D_{3h} symmetry) with all carbonyl ligands bonded terminally. Here the number of possible structures is more restricted. The structures in Scheme 2 may be derived from those in Scheme 1 only by the conversion of the ligand shell from the icosahedron into the anticubeoctahedron by cleavage of six icosahedral edges as shown in Fig. 5.

This interconversion is expected to be of higher energy than the librational mode postulated above and shown in Fig. 3.



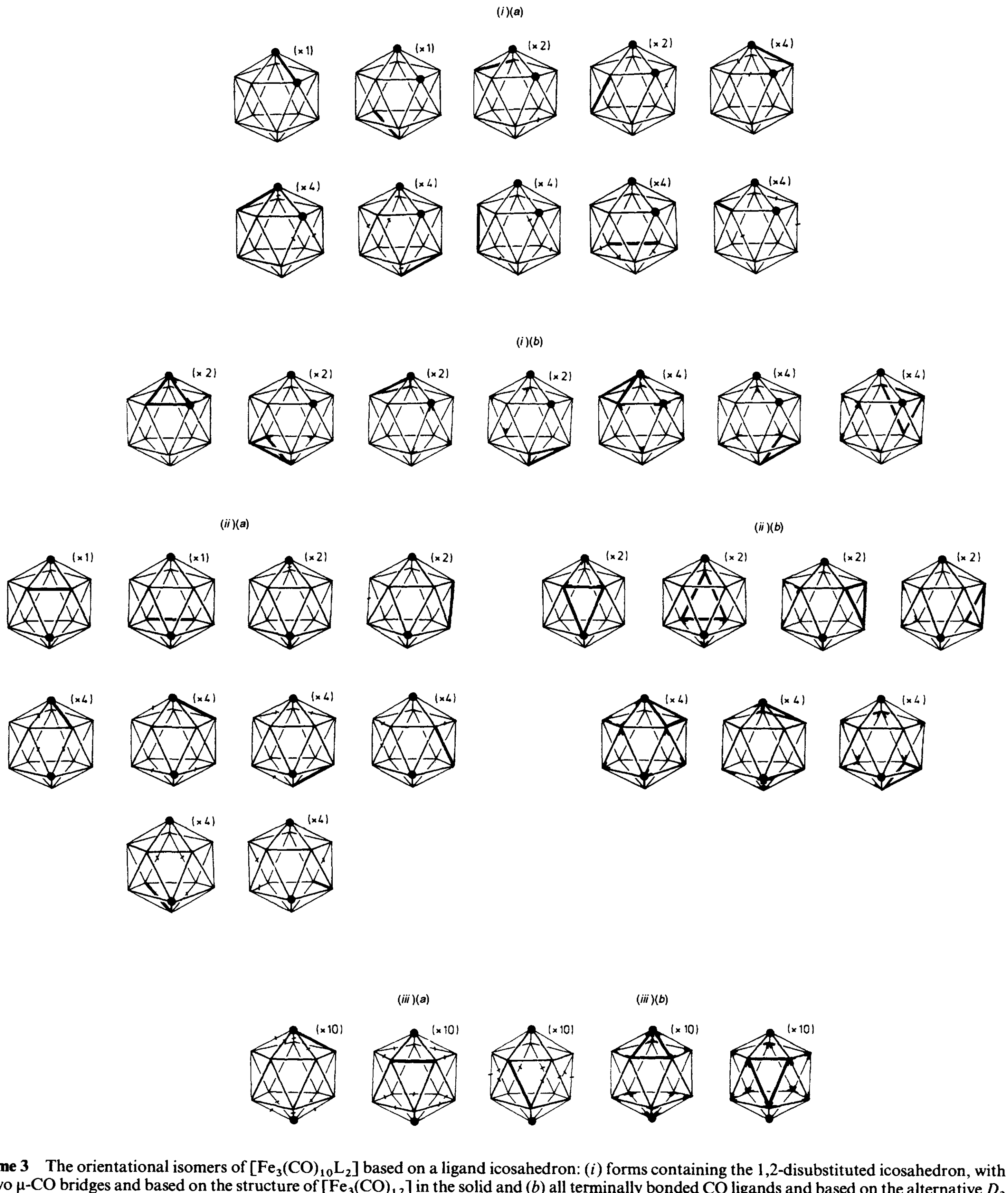
Scheme 2 The various isomers possible for [$Fe_3(CO)_{11}L$] based on an anticubeoctahedral array of ligands: forms derived from the C_{2v} (*a*) and D_3 isomer (*b*) of [$Fe_3(CO)_{12}$]

Nevertheless, this motion may also lead to isomerisation and the anticubeoctahedron may be regarded as a suitable complementary polyhedron for permutation of the vertices of the icosahedron. This mechanism of isomerisation is expected to act in concert with the librational motion described above and, as explained previously,[3,4,6–8] will vary in its contribution to the overall process.

Clearly, the same ideas may be extended to include the range of known substituted compounds [$Fe_3(CO)_{12-n}L_n$] (n = 2 or 3). In Scheme 3 we show the wide variety of forms available for the bis-substituted species [$Fe_3(CO)_{10}L_2$]. In this case, however, we must consider three different types of bis-substituted icosahedra. In Scheme 3(*i*) all isomeric forms are based on the 1,2-bis-substituted icosahedron shown in Fig. 6(*a*). All may be deemed to be orientational isomers (see above) since one may be converted into another merely by the reorientation of the Fe_3 triangle with respect to the 1,2-bis-substituted icosahedron and *vice versa*. Again the isomers are of two types. Those based on the parent C_{2v} form shown in Scheme 3(*i*)(*a*) and those based on the alternative D_3 form shown in Scheme 3(*i*)(*b*). In Scheme 3(*ii*) all the isomers are based on the 1,7-bis-substituted icosahedron [Fig. 6(*b*)] and again may interconvert by libration. It is important to appreciate that this set of orientational isomers cannot be converted into those of Scheme 3(*i*) by librational motion alone. Finally, in Scheme 3(*iii*) are listed the isomers based on the third possible substitution pattern for a bis-substituted icosahedron, *viz.* the 1,12 form [Fig. 6(*c*)]. The same criteria apply. All may be interconverted within the Scheme 3(*iii*) set by libration; none may be converted into those isomers in either 3(*i*) or 3(*ii*) by the librational process alone. Just as in the other sets, Scheme 3(*i*) and (*ii*), structures based on both C_{2v} and D_3 forms are possible.

Interconversion of representatives of one set [*e.g.* Scheme 3(*i*)] into another [*e.g.* Scheme 3(*ii*) or 3(*iii*)] can only occur by permutation of the vertices of the respective icosahedron, *i.e.* 1,2 $\rightleftarrows$ 1,7 $\rightleftarrows$ 1,12. This, we have argued,[6] can best occur *via* the anticubeoctahedral complementary geometry. This process of interconversion of the 1,2 to the 1,7 and to the 1,12 forms is illustrated for the parent icosahedron in Fig. 7. As emphasised above, we regard this as a higher-energy process than that of libration.

For the bis-substituted icosahedra with either the 1,2 or the 1,7 distribution of L, the five modes of polyhedral interconversion through the intermediate anticubeoctahedral geometry will not be degenerate. This aspect has been described previously and in detail for the intermediate cubeoctahedron in the rearrangement processes observed for [$M_3(CO)_{12}$] (M = Fe, Ru or Os)[6,8] and [$M_4(CO)_{12}$] and their relatives (M = Co, Rh or Ir).[4] Here it is sufficient to note that for these two forms the five modes are no longer degenerate and each mode is further split into two (see below). Two modes (C and D′) bring about the conversion of the 1,2 into the 1,7 form by separation of the two ligands L. These are shown in Fig. 8. The others,



Scheme 3 The orientational isomers of $[Fe_3(CO)_{10}L_2]$ based on a ligand icosahedron: (*i*) forms containing the 1,2-disubstituted icosahedron, with (*a*) two μ-CO bridges and based on the structure of $[Fe_3(CO)_{12}]$ in the solid and (*b*) all terminally bonded CO ligands and based on the alternative D_3 form; (*ii*) forms containing the 1,7-disubstituted icosahedron with (*a*) two μ-CO bridges and quasi-C_{2v} symmetry and (*b*) all terminally bonded CO and quasi-D_3 symmetry; (*iii*) forms containing the 1,12-disubstituted icosahedron with (*a*) and (*b*) as in (*ii*)

which are degenerate, ultimately lead to scrambling of the ten carbonyl ligands and thus fluxionality without isomerisation.

In the 1,7-bis-substituted species there is further removal of the degeneracy: two modes (A′ and D′) lead to the 1,12 form and two others (C′ and E) to the 1,2 form. The remainder lead to interchange of CO groups without isomerisation. In the 1,12 forms the five modes remain degenerate. Hence, carbonyl interconversion can only occur with isomerisation.

The relative stabilities of the three forms (1,2, 1,7 and 1,12) are not known, but it is realistic (on steric grounds) to assume that they lie in the order 1,2 < 1,7 < 1,12. The larger the ligand L the greater is the tendency for the two ligands to separate.

It is extremely important, at this point, to stress that the inclusion of the Fe_3 triangle into the ligand polyhedron has significant consequences for the vertex interchange positions if the ligand type is taken into account. For a bare icosahedron, *I* (numbered as in the key shown), all vertices are equivalent.

Table 1

Vertex	1	2	3	4	5	6	7	8	9	10	11	12
I	L	adj	adj	adj	adj	adj	low	low	low	low	low	anti
D_3	$M^1{}_{ax}$	$M^3{}_{ax}$	$M^2{}_{ax}$	$M^1{}_{eq}$	$M^1{}_{eq}$	$M^3{}_{eq}$	$M^2{}_{eq}$	$M^2{}_{eq}$	$M^1{}_{ax}$	$M^3{}_{ax}$	$M^3{}_{eq}$	$M^2{}_{ax}$
C_{2v}	$4T_{ax}$	B	$3T_{ax}$	$4T_{eq}$	$4T_{eq}$	$3T_{ax}$	$3T_{eq}$	$3T_{eq}$	$4T_{ax}$	$3T_{ax}$	$3T_{eq}$	B

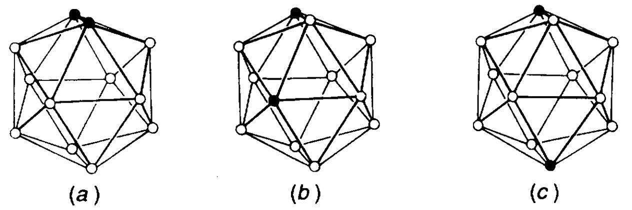


Fig. 6 The 1,2- (*a*), 1,7- (*b*) and 1,12-bis-substituted icosahedra (*c*)

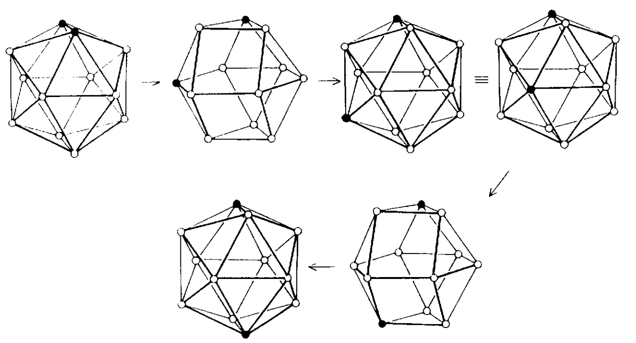


Fig. 7 One combination of modes for the conversion of the 1,2-bis-substituted icosahedron, through an anticubeoctahedral intermediate, into 1,7- and 1,12-bis-substituted icosahedra

Table 2

	Vertices	Mode	I	D_3	C_{2v}
(i)	1,2	C	1,10	4,2	6,3
(ii)	1,2	D′	1,8	1,11	3,6
(iii)	1,7	A	1,12	1,12	1,12
(iv)	1,7	D′	1,12	1,12	3,10
(v)	1,7	C′	1,6	3,7	3,7
(vi)	1,7	E	1,3	3,7	3,7

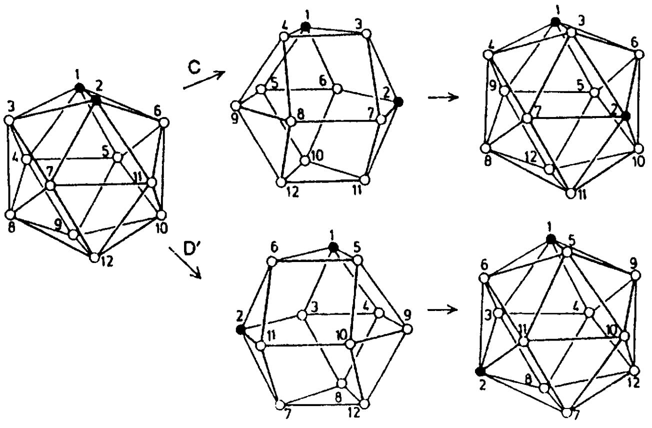


Fig. 8 The two modes of interconversion of the 1,2-bis-substituted icosahedron into the 1,7 form

Once vertex 1 has been assigned (L) a high degree of degeneracy exists. Hence, vertices 2–6 are equivalent [adjacent (adj)] as are 7–11 [lower ring (low)]. Vertex 12 is unique [antipodal (anti)].

If a D_3 isomer of $[Fe_3(CO)_{12}]$ is considered, the vertices are further distinguished by being either axial or equatorial (with respect to an Fe atom) and by the metal they are associated with. For example, if vertex 1 is axial, two kinds of equatorial ligand exist: those associated with the same metal (vertices 4 and 5) or those associated with a different metal (vertices 6–8 and 11).

The picture is further complicated for the C_{2v} isomer. Not only are there now three different types of ligands initially (axial, equatorial or bridging), but the metals are also of two different types: metal 1 has four terminal ligands, whereas 2 and 3 have three terminal (T) and one bridging (B) ligand. The information may be summarised as in Table 1. Operation of the modes described in the text above leads to the vertex changes in Table 2. If the vertex types are not taken into account, then modes C and D′ convert vertices 1 and 2 into a 1,7-type arrangement (2,4 and 3,6 would be equivalent to 1,7). However, if vertex types are taken into account, then only the I and D_3 forms are truly equivalent to a 1,7-substitution pattern. Hence, in (iv), 3,10 is not fully equivalent to 1,12 and in (v) and (vi) 3,7 is not fully equivalent to 1,2, unless the vertex types are ignored.

In Scheme 4 are illustrated the isomers based on an anticubeoctahedral ligand shell. Again, these may be derived simply from their icosahedral counterparts by the opening of six appropriate edges.

Extension of these ideas to the tris-substituted derivatives follows exactly the same pattern. Here, because of the degree of substitution, the pattern of substitution in this icosahedron is far more complicated, with 1,2,3, 1,2,4, 1,7,8, 1,7,9 and 1,x,12 (x = 2–11).* Separation of these polyhedra into the four sets shown in Scheme 5 allows a clearer view of their relationship. All members in Scheme 5(*i*) may interconvert, *etc.*, but interconversion of these into those of set (*ii*), (*iii*) or (*iv*) requires polyhedral rearrangement of the sort explained earlier and shown for a tris-substituted icosahedron in Fig. 9.

These examples of mono-, bis- and tris-substituted derivatives may serve to illustrate the complexity of isomer distribution in the substituted dodecacarbonyls of Fe, Ru or Os. Clearly, as the degree of substitution is increased (until n = 6) the problem will become increasingly complex. For certain ligands (*e.g.* R_3P) which do not generally form bridges and tend preferentially to occupy axial rather than equatorial sites, the problem simplifies greatly. Nevertheless, we should emphasise that although these forms are not observed as stable structures, the possibility that they serve as intermediates in any fluxional or isomerisation steps cannot be ignored.

The number of isomers for n = 4–6 can be derived in the same manner. In general, the number of distinct isomers increases and their symmetry is lower than for less-substituted species.

Conclusions

The mechanisms by which isomer interconversion may occur within the species $[Fe_3(CO)_{12-n}L_n]$ are moderately easy to visualise and understand within the terms of the ligand polyhedral model. They may be conveniently sub-divided into two

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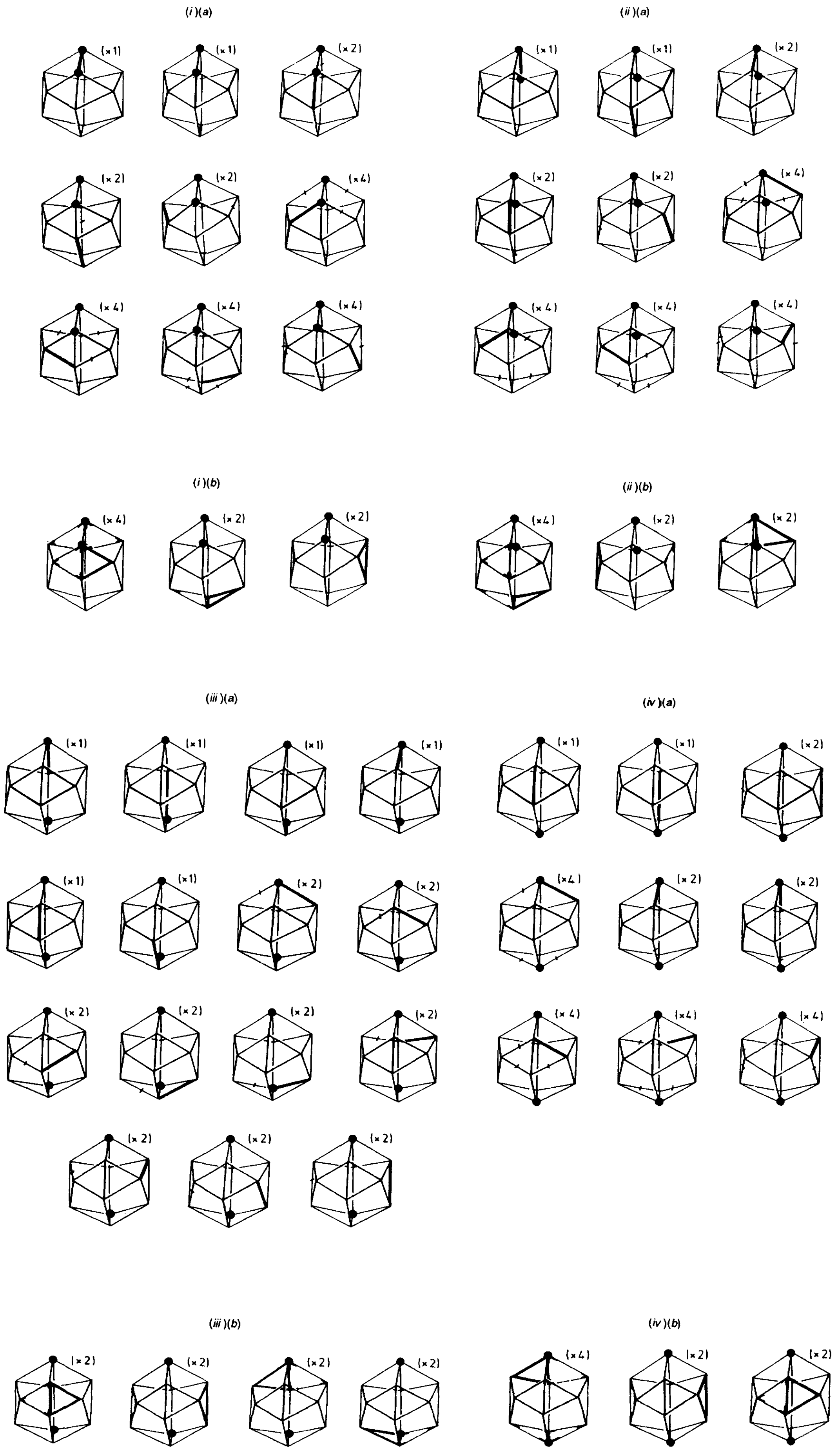
* 1,2,4 ≡ 1,2,7, 1,2,8 ≡ 1,7,8, 1,2,9 ≡ 1,2,12 and 1,2,12 ≡ 1,x,12 (irrespective of value of x).



(*i*)(*a*)

(*ii*)(*a*)

(*i*)(*b*)

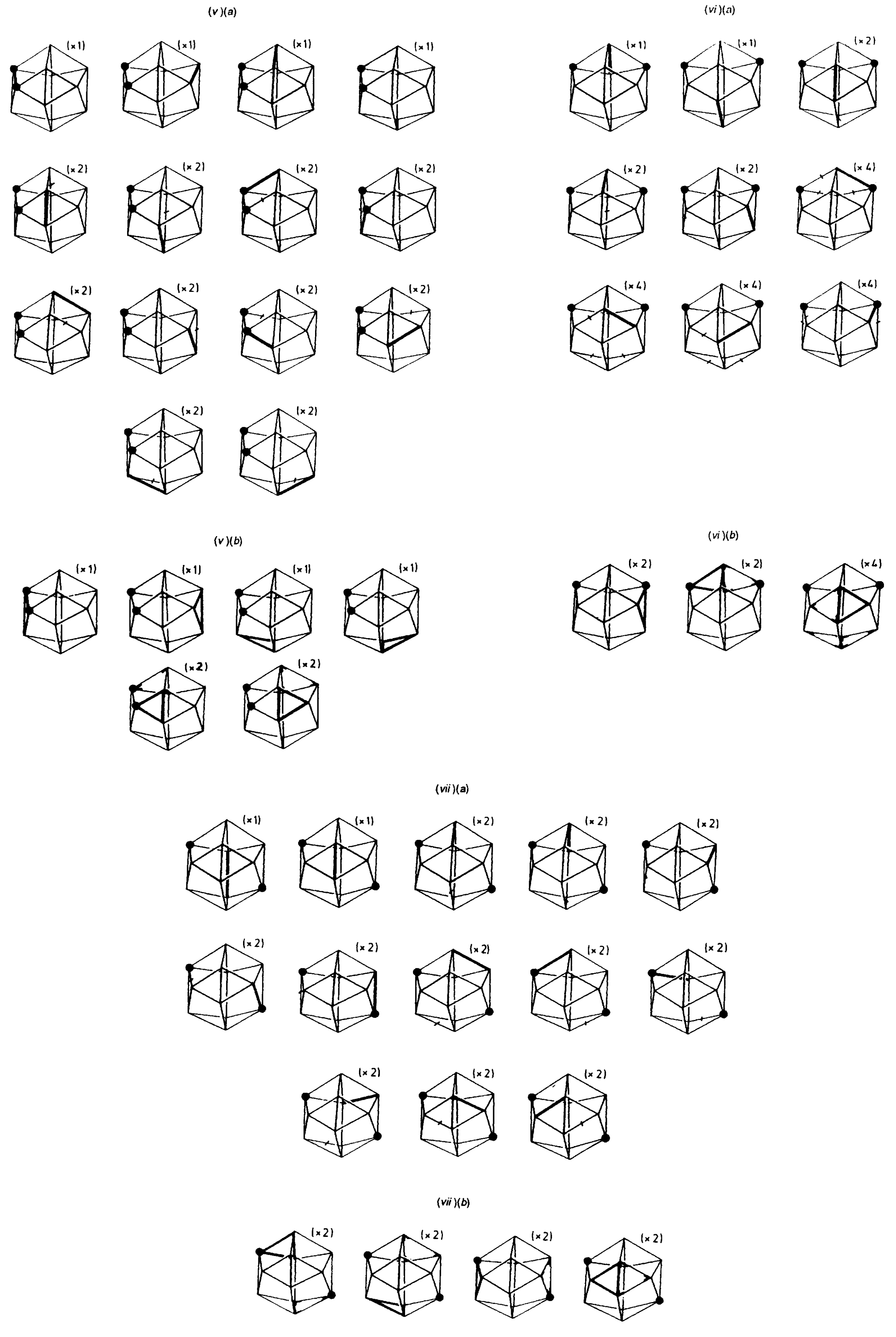
(*ii*)(*b*)

(*iii*)(*a*)

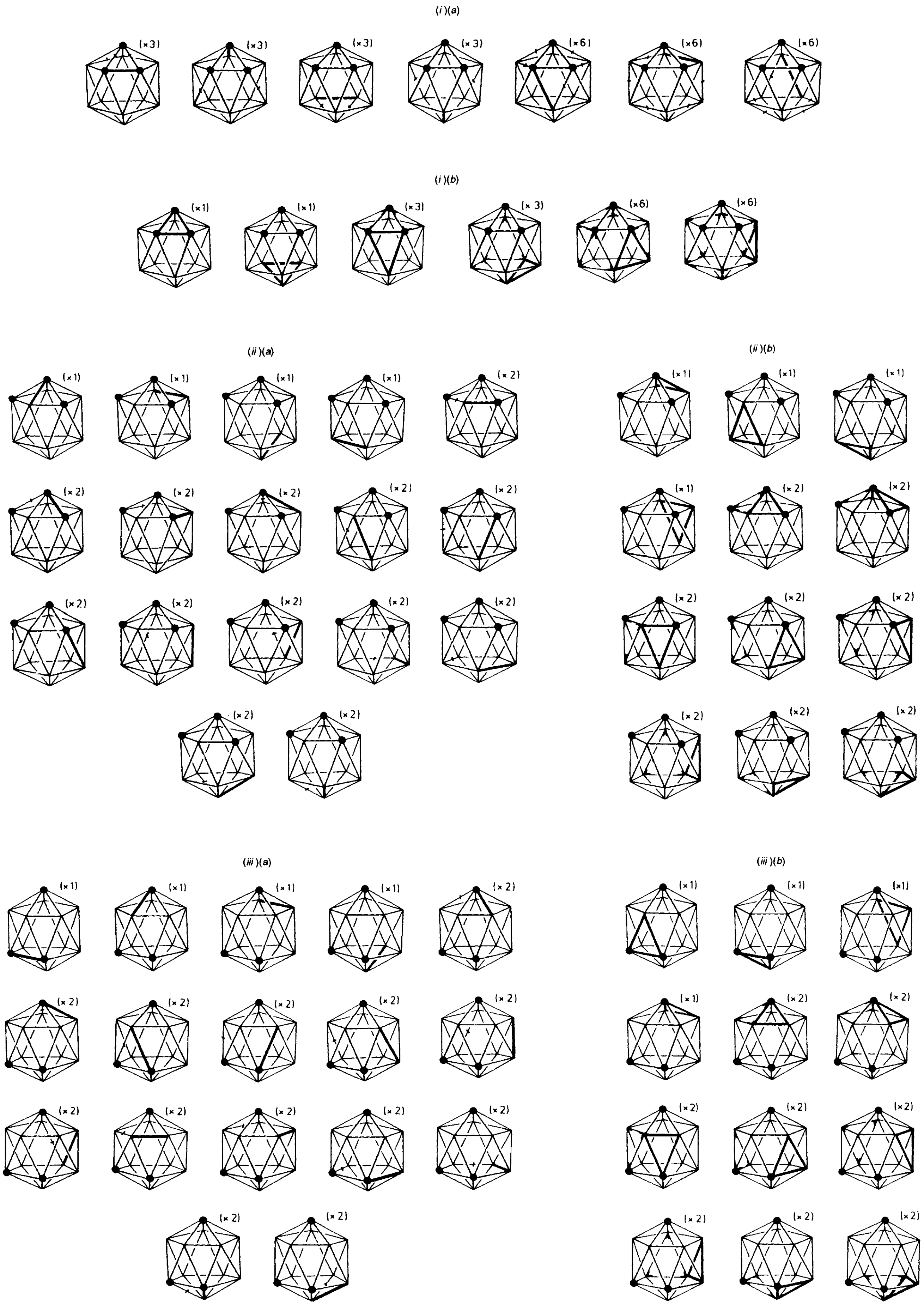
(*iv*)(*a*)

(*iii*)(*b*)

(*iv*)(*b*)



Scheme 4 The various isomers possible for [$Fe_3(CO)_{10}L_2$] based on an anticubeoctahedral ligand shell, derived from disubstituted icosahedral precursors. For 1,3, 1,7 and 1,8 substitution every edge and face is unique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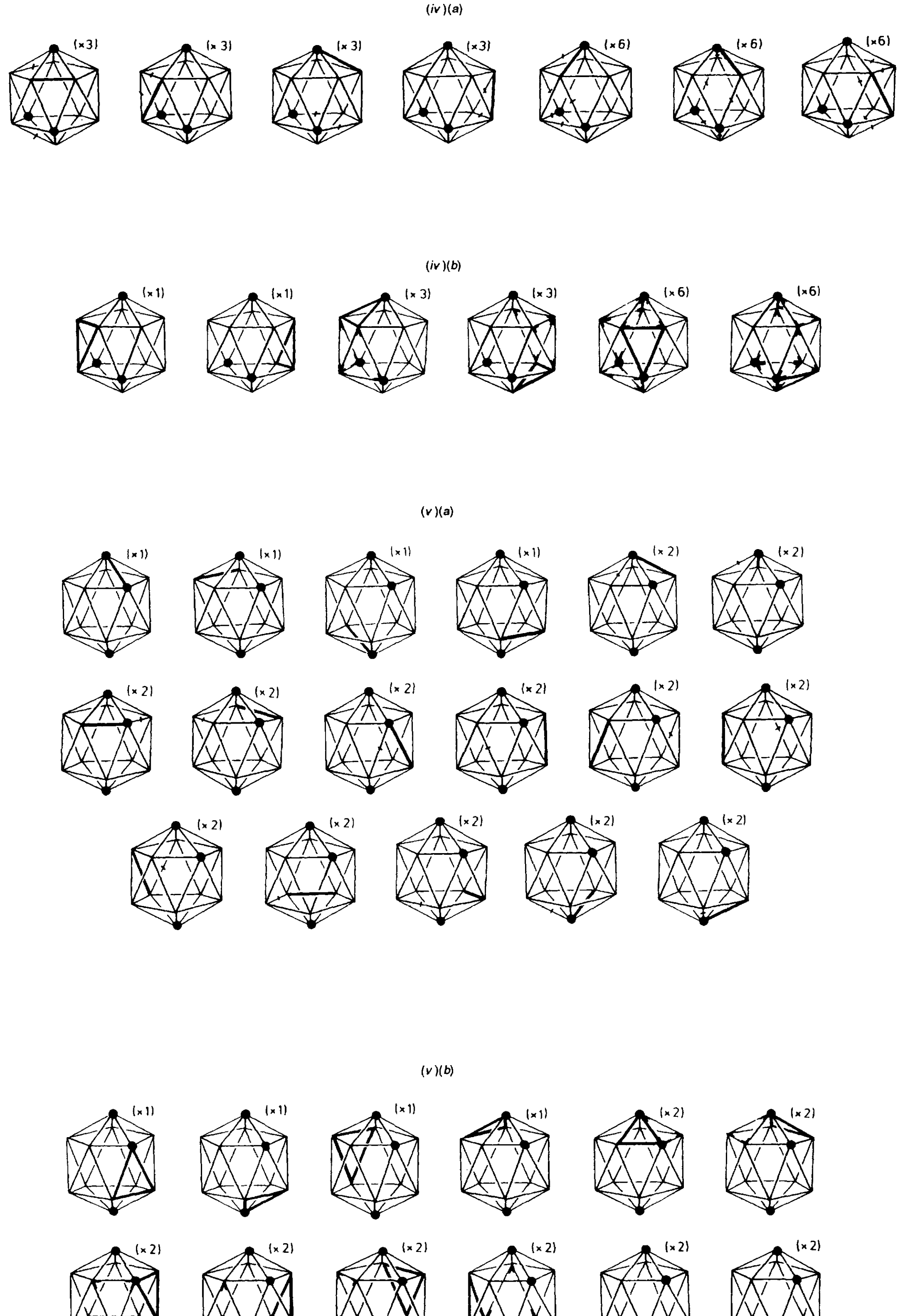

Scheme 5 The orientational isomers of [$Fe_3(CO)_9L_3$] based on an icosahedral ligand polyhedron: (*i*) those with 1,2,3-trisubstituted icosahedron with (*a*) two μ-CO bridges and based on the structure of [$Fe_3(CO)_{12}$] in the solid and (*b*) with all terminally bonded CO ligands and based on the alternative D_3 form; (*ii*) those with a 1,2,4-trisubstituted icosahedron and with (*a*) two μ-CO bridges and quasi-C_{2v} symmetry and (*b*) all terminally bonded CO and quasi-D_3 symmetry; (*iii*) those with a 1,7,8-trisubstituted icosahedron and (*a*) and (*b*) as in (*ii*); (*iv*) those with a 1,7,9-trisubstituted icosahedron and (*a*) and (*b*) as in (*ii*); (*v*) those with a 1,*n*,12-trisubstituted icosahedron and (*a*) and (*b*) as in (*ii*)

categories: (*i*) those which differ in the orientation of the Fe_3 triangle within the ligand shell and, (*ii*) those which differ in the arrangement of the ligands (CO and L) within the ligand shell itself. We deem these to be orientational (*i*) and geometrical (*ii*) isomers. Under heading (*ii*) different isomers may be available because Of the different polyhedral forms adopted by the ligand shell (*i.e.* icosahedral or anticubeoctahedral).

Interconversion between orientational isomers occurs by libration of the Fe_3 triangle within the ligand envelope. Isomerisation of the geometrical forms occurs *via* a polyhedral

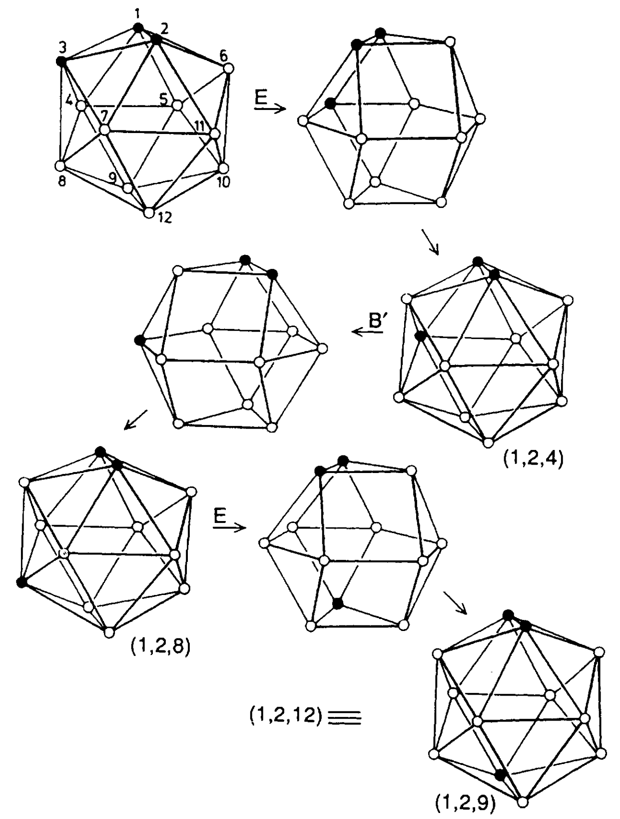

Fig. 9 One combination of modes for the interconversion of the 1,2,3-, 1,2,7-, 1,2,8- and 1,2,12-tris-substituted icosahedra

rearrangement. These two motions will act in a concerted manner and are not independent. The factors which determine which isomers are preferentially formed are less easily defined. There is no doubt that a dominating contribution to the difference in energies between isomers is the steric constraint of the ligand envelope. The formation of equatorial forms only of $[Fe_3(CO)_{11}L]$ may be electronic in origin, but the adoption of preferential equatorial forms of $[Fe_3(CO)_{10}L_2]$ may also be a function of the type of substitution within the ligand shell (*e.g.* 1,2, 1,7 or 1,12) itself. This is more apparent with other species such as $[M_4(CO)_{12-n}L_n]$.

In this paper we have attempted to reveal and unravel some of the complexities of cluster isomerism in the systems $[Fe_3(CO)_{12-n}L_n]$ and to lay down some ground rules for a better appreciation of this widespread and apparently complicated phenomenon. We would again emphasise that the approach is not restricted to these trinuclear iron cluster carbonyls, but is general and may be applied to a wide range of cluster species.

Acknowledgements

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